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EEB BRANCH REVIEW

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RD REQUESTED COMPLET	TON DATE 9-4-84	
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RD ACTION CODE/TYPE	OF REVIEW 336/Amendment	
		
TYPE PRODUCT(S): I,	D, H, F, N, R, S Fungicide	
DATA ACCESSION NO(S)		
PRODUCT MANAGER NO.	H. Jacoby (21)	
PRODUCT NAME(S)	Bravo 500	
		
COMPANY NAME		
SUBMISSION PURPOSE _	Submission of Registrant's Response Concerning	.
_	Aquatic Field Study	
_		
SHAUGHNESSEY NO.	CHEMICAL, FORMULATION	% A.I.
081901	Chlorothalonil	

Chlorothalonil Bravo 500

100 Submission Purpose

With this submission SDS Biotech Corporation provided additional information for their 1982 Aquatic Field Study with Bravo 500. EEB has revalidated the study in light of the additional information and a site visit by the reviewer. In addition, EEB will assess the hazard of the major agricultural crops based on the results of this field study.

101 Hazard Assessment

101.1 Discussion

The studies provided by the registrant indicate that chlorothalonil:

1. Is very highly toxic to aquatic organisms.

Bluegill $LC_{50} = 62 \text{ ppb}$ Rainbow trout $LC_{50} = 32 \text{ ppb}$ Daphnia magna $LC_{50} = 70 \text{ ppb}$ Channel Catfish $LC_{50} = 43 \text{ ppb}$ MATC for Fish >3 <6.5;

- Is persistent, (one-half life = 35 days in water);
- 3. Will transport from a treated field to an adjacent water body under typical agricultural conditions. Mode of transport will be both drift and runoff as shown in the field study;
- 4. Chlorothalonil will occur as residues in pond sediment. Measured levels in the top 5-6 cm of sediment reached over 50 ppb. It is assumed that the residues in the top 1 cm would be substantially higher than those measured; possibly more than 5 times higher.

$$5 \times 51 = 255 \text{ ppb}$$

even measured residue concentrations of 20 ppb mean the concentration in the top 1 cm was 100 ppb;

5. Will probably not occur in the water column at levels high enough to be hazardous to aquatic organisms.

The uses for which this hazard assessment is being prepared include corn, wheat, soybeans and some smaller acreage crops. These crops are grown throughout the United States, especially the midsouth, the mid west and California.

101.2 Likelihood of Adverse Effects to non-target Organisms

As was stated in the 5/1/80 review, these uses are not likely to affect terrestrial organisms (birds, mammals or reptiles).

The field study shows that under typical use conditions chlorothalonil could transport to aquatic habitats adjacent to treated fields and occur in the sediment at levels greater than fish and aquatic invertebrates LC_{50} 's. It is not likely to remain in the water column so it will not be available to free-swimming aquatic organisms such as fish.

Chlorothalonil is likely to have an acute adverse effect on various benthic organism groups. Such groups include:

- 1. The unicellular organisms which feed on detritus, bacteria and other unicellular organisms. These in turn become food for higher animals.
- 2. The flatworms and roundworms. They creep over the bottom feeding on smaller organisms.
- 3. The rotifers, some of which are found in the sediments of shallow shore-zones and in the bottom deposits of deep water.
- 4. The segmented worms including the oligochaets and hirudinea. Some of these feed on detritus and others are carnivorvours. These worms in turn became food for fish.
- 5. The Arthropods, Arachnids, Insects and Molluscs all have representatives which dwell in the sediment. Most are carnivorous, although some feed on detritus.

These benthic organisms consume detritus, algae and each other. They in turn become food for higher animals and man. They form an important part of the food web and disruption to these groups could result in disruption to the entire aquatic community.

The above discussion is based on toxicity data generated under laboratory conditions where chlorothalonil was maintained in solution. There are no data available showing how toxic or non-toxic chlorothalonil is when it is bound to sediment. Until such data are available it is assumed that chlorothalonil is having an adverse effect on benthic organisms.

It is also likely that bottom-feeding fish such as catfish would ingest sediment and detritus associated with chlorthalonil, residues. They could be exposed to levels greater than the fish $\rm LC_{50}$'s mentioned earlier.

101.3 Endangered Species Considerations

The use of chlorothalonil on major agriculture crops is not likely to be having an adverse effect on terrestrial organisms.

However, it is possible that the use of chlorothalonil on major crops could have an adverse effect on endangered invertebrates and possibly endangered fish. The cluster review for major row crops mentions 2 fish and several mussels that are associated with these use sites.

The two fish are the slackwater darter and the wouldfin.

Slackwater Darter (Etheostoma boschungi)

The distribution of this threatened species is known in five tributary streams to the south bend of the Tennessee River on both sides of the Tennessee-Alabama State line. These are: Buffalo River, Lawrence County, Tennessee; Shoal Creek, Lawrence County, Tennessee; Flint River, Madison County, Alabama; Swan Creek, Limestone County, Alabama; and Cypress Creek Watershed, Wayne County, Tennessee, and Lauderdale County, Alabama.

To preclude jeopardy, the following reasonable and prudent alternatives are recommended: eliminate aerial applications of implicated pesticides or provide a buffer zone of 100 yards between aerially treated areas and the aquatic habitat of this species, and prohibit the use of implicated pesticides by ground application closer than 20 yards from the edge of the aquatic habitats of this species.

Woundfin (Plagopterus argentissimus)

The present distribution of the wouldfin extends about 40 miles above and 40 miles below the Virgin Narrows on the Virgin River in Utah, Arizona, and Nevada.

To avoid jeopardy to the wouldfin we suggest the following reasonable and prudent alternative: prohibit the use of those chemicals toxic to fish on irrigated lands which provide return flows directly into the Virgin River drainage 40 miles either side of the Virgin Narrows.

Mussels

Alabama lamp pearly mussel Lampsilis virescens Appalachian monkeyface pearly mussel Quadrula sparsa Cumberland monkeyface pearly mussel Q. intermedia Dromus dromas Dromedary pearly mussel Birdwing pearly mussel Conradilla caelata Cumberland bean pearly mussel Villosa trabalis Green blossom pearly mussel Epioblasma torulosa gubernaculum Turgid blossom pearly mussel E. turgidula E. walkeri Tan riffle shell Pale lilliput pearly mussel Toxolasma cylindrella Fusconaia cuneolus Fine-raged pigtoe F. edgariana Shiny pigtoe

All these mussel are characteristically found in the headwaters or small rivers in the middle and upper drainages of the Cumberland and Tennessee Rivers. Should runoff of chlorothalonil into a stream supporting one of these endangered mussels occur, dilution may not be sufficient to eliminate hazards. According to the cluster review opinion, steps must be taken to alleviate hazards to endangered mussels. To preclude jeopardy, the following is recommended: eliminate aerial application of chlorothalonil or provide a buffer zone of 100 yards between aerially treated areas and the aquatic habitat of the species, and prohibit the use of Bravo 500, by ground application closer than 20 yards from the edge of the aquatic habitat.

There are no endangered insect species adjacent to the major agricultural crops for which chlorothalonil is registered (corn and soybeans).

101.4 Adequacy of Toxicity Data

The data available were adequate to perform this hazard assessment.

Additional information was provided for the Aquatic field monitoring study conducted in 1982. A final validation was performed on this study. The results showed that chlorothalonil will transport from a typical soybean field under normal rainfall and agricultural conditions via soil erosion. It showed that chlorothalonil will bind to the hydrosoil and will not be found in the water column. When applied by ground application, the study showed that chlorothalonil will also reach adjacent aquatic habitats solely via drift. In the reviewer's opinion, no fish mortality was caused by exposure to chlorothalonil. The study fulfills the requirements for an aquatic monitoring study addressing the fate of chlorothalonil when applied to a major agricultural crop such as soybeans. It would not fulfill the requirements for a field study on such use sites as orchards or rice.

101.5 Labeling

No specific label was included with this data. The labeling specified in the EEB Disciplinary Review of the Registration Standard is appropriate based on this hazard assessment.

103 Conclusions

EEB has completed on incremental risk assessment (3(c)(7) Finding) of the use of chlorothalonil on major agricultural crops such as corn and soybeans. Based on the available data EEB concludes that the uses of chlorothalonil provide for:

- 1. no adverse effects to terrestrial non-target organisms;
- 2. no adverse effects to most fish;
- 3. possible adverse effects to non-target benthic organisms and bottom-feeding fish; and
- possible adverse effects to endangered fish and mussel species.

To preclude jeopardy to endangered fish and mussel species, see the directions in secton 101.3 Endangered Species Considerations of this review.

Daniel Rieder 8/14/84

Daniel Rieder Wildlife Biologist Section 2

Section 2 Ecological Effects Branch, HED

Morm Cook
Section Head
Ecological Effects Branch, HED

Clayton Bushong Branch Chief

Ecological Effects Branch, HED

DATA EVALUATION REPORT

1. CHEMICAL: Chlorothalonil

2. FORMULATION: Bravo 500

Shaughnessey Number: 081901

3. CITATION: Shultz, Stephen K. 1982. Aquatic Field study with Bravo 500. An unpublished study submitted by Diamond Shamrock. Data Acc #071552.

4. REVIEWER: Daniel Rieder

Wildlife Biologist

EEB/HED

5. REVIEW DATE: 7/11/84

6. TEST TYPE: Aquatic field monitoring study.

- 7. RESULTS: The field study showed that chlorothalonil will transport from a typical soybean field under normal rainfall conditions via soil runoff. It showed that chlorthalonil will bind to soil and will not be found in the water column. When applied by ground application, there was evidence of drift since residues occurred in the control pond after treatment. The caged fish apparently did not die from chlorothalonil.
- 8. <u>CONCLUSIONS</u>: This fulfills the requirements for an aquatic field monitoring study addressing the fate of chlorothalonil when applied to an agricultural crop such as soybeans.

METHODS

The field study was conducted at St. Michaels, Md. Bravo 500 was applied 3 times to 8.3 acres of cropland planted in soybeans. Application was by ground vehicle at a rate of 2.75 pints (1.4 lbs a.i.) per acre. Application dates were September 1, 15, and 29, 1981.

On a predetermined schedule (each spray day, 3 days and 10 days after each spray day and 24 days after the third spray for a total of 10 sampling days) samples of pond water, pond sediment, and caged bluegill an channel catfish were taken. After significant rainfall, runoff collecting bottles were collected and replaced in the two main runoff channels of the spray field. Additionally 1 day and 3 days after each of seven runoff events, pond water from both ponds were collected. All collected samples were packed on dry ice for shipping.

A 1.5 acre pond was used as a control, the experimental pond was 3.8 acres. Eight cages were placed in each pond, is sets of two. One cage in each set was for bluegill, the other was for catfish. A hundred fish were placed in each cage. These fish werre observed for mortality and sampled for residues. Six catfish and 6 bluegill were sampled from each cage each sampling day.

Results

The Exposure Assessment Branch (EAB) concluded that the study was well conducted and satisfies the aquatic field dissipation requirement. According to the EAB review (5/11/84) runoff of chlorothalonil from treated fields is expected with greater residue amounts associated with soil rather than with water.

Fish: The caged fish apparently did not experience acute effects from exposure to chlorothalonil. The mortality that did occur did not correspond to any particularly high residue levels in the pond. See the following table:

FISH MORTALITY

' Treatment		Experimental Pond Number of Mortalities*		Control Pond Number of Mortalities*	
Number	Day	Bluegill	Catfish	Bluegill	Catfish
Pre-treatment	-	14	0	3	0
One	0	0	0	0	. 0
•	3	0	0	0	,0
	10	0	0	0	0
Two	0	2	0	1	. 0
= 11 = 1	3	0	0	Ó	1
	10	0	0	. 1	0
Three	0	0	0	0	. 0
	3	0	0	0	0
	10	41	0	1	0
	24	2	0	0	0

* Total cumulative mortality at all four sampling stations (pre-treatment)
Total mortality at all four sampling stations per day (post-treatment)

Since the residues detected were far below the levels expected to cause mortality, the mortalities were attributed to natural causes, or stress from confinement. No deaths in the native fish populations were observed.

No residues of chlorothalonil were detected in fish in either the experimental or control pond. DS-3701, the major degradate, was detected in catfish following the second application.

Residues: Maximum values of 0.7 ppb for the experimental pond and 1.3 ppb for the control pond were found in pretreatment pond water samples. After treatment, maximum residues were 0.6 ppb and 1.1 ppb in the experimental and control pond water respectively.

The highest residues found in sediment were 51 ppb and 31 ppb in the experimental pond and control pond respectively.

Figure 1 is a graph showing maximum sediment residues at the 3 sampling sites in the control pond. Figure 2 shows maximum residues of chlorothalonil in the experimental pond sediment. Figures 3 through 12 are maps of the study site showing the maximum residue levels at the sampling sites on each day of sampling.

REVIEWERS EVALUATION

There are several points which need to be addressed.

- 1. According to the report, the field was a worst case situation as far as runoff is concerned because of the way the rows ran (i.e. prependicular, to the pond). A site inspection revealed that the field was so level that it would matter little which way the rows ran. And since most of the runoff left via the two main channels, the lay of the rows actually probably reduced runoff. I consider the site to be very typical of soybean fields and certainly not a worst case.
- 2. The water residues found before treatment cast doubt on the validity of the chemical analysis method; at least for detecting water residues.
- 3. The ratio of field size to pond size was not what I would have preferred. A smaller pond, resulting in less dilution would have been more desireable.
- 4. On the day of the site inspection there was water flowing into the pond from the woods and the area to the northeast. This suggests that dilution could reduce any residues occurring in the pond and cause outflow of residues bound to suspended sediment.
- 5. The caged fish, not withstanding the mortality, show the levels in the pond probably never got over 30-40 ppb for any substantial length of time.
- 6. The residues in the control pond sediment after-treatment were considered to have been the result of drift.

- 7. Since the residues in the experimental pond sediment were higher than in the control, rumoff and drift were both probably responsible.
- 8. The runoff water and runoff soil both contained chlorothalonil residues on several occassions. See figures 13-16. The runoff soil contained very high levels of chlorothalonil, as high as 235.1 ppm.
- 9. The sediment was sampled to a depth of 5-6 cm. Presumably the sediment that contained chlorothalonil would be deposited as a thin layer on the surface of the pond bottom. So the concentration in this top thin layer would be substantially higher than the measurements show.

Summary:

- Chlorothalonil will drift to areas adjacent to treated fields even if it is applied by ground equipment. It is likely that drift was a major source of residues in this study.
- Chlorothalonil will bind to soil and leave a treated field via runoff under standard soybean growing conditions.
- Chlorothalonil will not occur in the water column for long.
- Chlorothanonil will find it's way to the sediments of ponds adjacent to treated fields either through drift or runoff. These residue levels could exceed the fish 96-hour $\rm LC_{50}$'s. However the residues apparently drop to non-detectable levels within a few days.

Conclusions

Category - Meets requirements for a field study addressing the fate of chlorothalonil when applied to a typical soybean field adjacent to a pond.

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* T * *		Shaughnessy No.: 081901		
		Date out EAB:	1 1 MAY 1984	
To:	H. Jacoby Product Manager 12 Registration Division (TS-76)	- .		
From:	Samuel M. Creeger, Chief Environmental Chemistry Review Exposure Assessment Branch Hazard Evaluation Division (5)			
Attache	ed, please find the EAB review	of:		
Reg./Fi	ile No.: 50534-8			
Chemica	al: Chlorothalonil			
Type Pr	roduct: F		•	
Product	Name: BRAVO 500	•		
Company	Name: SDS Biotech Corp.		,	
Submiss	sion Purpose: review aquatic	field dissipation :	study	
ZBB Cod	de: other	Action Code:_	400	
	: 1/27/84	EFB No.: 4180)	
Date Co	ompleted: 1984	TAIS (Level II	Days	
Deferra	als To:	62	3	
X	Ecological Effects Branch			
	Residue Chemistry Branch			
	Toxicology Branch	•	•	

1.0 INTRODUCTION

Diamond Shamrock has submitted an aquatic field dissipation study with chlorothalonil. Acc. No. 071552.

2.0 Bravo 500: chlorothalonil: DS-2787 2,4,5,6-tetrachloroisophthalonitrile

3.0 DISCUSSION

This study was conducted to determine the potential effects on the aquatic environment - water, sediment, and fish - as a result of the runoff of chlorothalonil and its degradation products from treated soybean fields.

A 3.8 acre experimental pond and a 1.5 acre control pond were selected in St. Michael's, MD. Approximately 8.3 acres were planted with soybeans. Chlorothalonil was applied using ground boom techniques. The application rate was 2.75 pt product per acre and chlorothalonil was applied every 14 days for a total of three applications. This rate is the maximum recommended label rate on soybeans.

Runoff was monitored during each significant rainfall at two runoff channels between the test field and the experimental pond. In the ponds, 4 stations were established and each contained separate cages with 100 bluegill sunfish or 100 channel catfish. Station 4 was restocked on day 10 after second treatment because fish escaped from the cage.

Before and after treatments, pond water (surface and bottom) and sediment were collected from both ponds along with native bluegill sunfish and non-native sunfish and catfish from experimental pond. Non native fish were sampled before placement into control pond and experimental pond. Pond water from both ponds was sampled for water quality analysis, temperature and light penetration.

Residues of chlorothalonil (DS-2787) and its degradation products 4-hydroxy-2,5,6-trichloroisophthalonitrile (DS-3701), 3-cyano-2,4,5,6-tetrachlorobenzamide (DS-19221), trichloro-3-carboxybenzamide (DS-46851), 3-cyano-trichlorobenzamide (DS-47524) and 3-cyanotrichlorohydroxybenzamide (DS-47525) were analyzed for in samples of pond water, pond sediment, runoff water, runoff soil and fish.

Results

Test site description, sampling schedule, water quality analyses, meteorological data during application, rainfall recordings and, sediment and soil analyses are all given in the Attachment.

Chlorothalonil and its degradation products were found in field runoff in both water and soil. These data indicate generally higher residues in soil than in water. Table 1 summarizes these data.

Pond water analyses indicated residues of chlorothalonil during the pretreatment period. Post treatment analysis indicated random findings of chlorothalonil and its degradation products. No residue of chlorothalonil was greater than 0.7 ppb in the experimental pond. These results are summarized in Tables 2 and 3.

Chlorothalonil and its degradation products were found in pond sediment for both pre- and post-treatment periods from both control and experimental ponds. These residue values were generally low and random in occurrence. Table 4 summarizes these results.

Residue values in fish were generally non-detectable. One sample of bluegill sunfish indicated residues of one degradation product before application. Post-treatment residues of chlorothalonil were not detected in catfish or sunfish from the experimental pond. Residues of degradation products were sporadic and low in these same fish. These data are summarized in Table 5.

Fish mortality was observed on day 10 after third treatment when 41 sunfish were found dead. No other significant mortalities took place. Because of the generally low levels of chlorothalonil residues, disease was thought to have caused these deaths. Table 6 shows these data.

4.0 CONCLUSIONS and RECOMMENDATIONS

The study was well conducted and satisfies the aquatic field dissipation requirement. No significantly large residues of chlorothalonil or its degradation products were found in fish or pond samples. Runoff of chlorothalonil from treated field is expected with greater residue amounts associated with soil rather than water runoff.

EAB defers to EEB to comment on any toxicological significance to non target species as a result of these residue levels.

Richard V. Moraski Review Section No. 1